

Methane-*n*-Butane-Water System in Two-and Three-Phase Regions

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Methane-*n*-Butane-Water System in Two- and Three-Phase Regions

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The compositions and specific volumes of the coexisting phases of the methane-*n*-butane-water system were determined experimentally in the two-phase and three-phase regions at temperatures of 100°, 160°, 220°, and 280° F. and pressures to 3000 pounds per square inch absolute. The distribution of the three components between the phases may be used to predict the water content of hydrocarbon phases and solubility of gases in water. The presence of water in the methane-*n*-butane system shifts the composition of the dew point mixture at a given temperature and pressure by as much as 8%. Equilibrium constants relating the concentration ratios between the several phases are presented.

SINCE water is present in natural gas and petroleum reservoirs, quantitative phase equilibria data in the hydrocarbon-water systems are of engineering value. Considerable data on the formation of solid hydrates have been presented in some detail (3, 6, 16, 17, 32, 42, 43, 49). Table I lists the hydrocarbon-water systems reported in the literature. In most cases the data available cover only one of the phases present. Table I also includes inorganic gases and water at high pressure. The work reported here consists of an experimental investigation of the methane-*n*-butane-water system in the three-phase region at temperatures of 100°, 160°, 220°, and 280° F. and pressures extending to the three-phase critical pressures. In the two-phase region, data were obtained at pressures of 2000 and 3000 pounds per square inch absolute.

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EXPERIMENTAL APPARATUS AND METHODS

Controlled compositions of methane, *n*-butane, and water were agitated in a pressure cell at constant temperature and pressure. Samples of each phase were withdrawn into pycnometers by mercury displacement. Analyses were made by adsorption of the water and by density measurements of the hydrocarbon vapor.

A schematic drawing of the equilibrium apparatus is shown in Figure 1. The equilibrium cell, of approximately 1000 cc. volume, was essentially the same as that described by Chaddock (5) and was provided with the following: (a) glass window for observation of phase behavior and liquid levels, (b) three sampling ports, (c) mercury port, and (d) stirring motor with stirring mechanism in the cell. The three pycnometers had a capacity of about 50 cc. each and weighed about 800 grams. The equilibrium cell, pycnometers, valves, and tubing were surrounded by an air bath, which air was agitated by a fan and heated with two heaters of approximately 500- and 1000-watt capacity each. The pressure was supplied with a hand-operated pump using mercury as the confining fluid. The temperature of the cell was measured by a pair of calibrated copper-constantan thermocouples embedded in the wall of the cell, and an additional thermocouple was used to measure the temperature of the air bath. The temperature of the cell proper was maintained within $\pm 0.2^\circ$ F. of the value reported. The pressures were read by means of two calibrated Bourdon gages. In the three-phase region a 0-to-1000 and a 0-to-3000 pounds per square inch gage was used. In the two-phase region a 0-to-3000 and a 0-to-5000 pounds per square inch gage was used. At pressures below 1000 pounds per

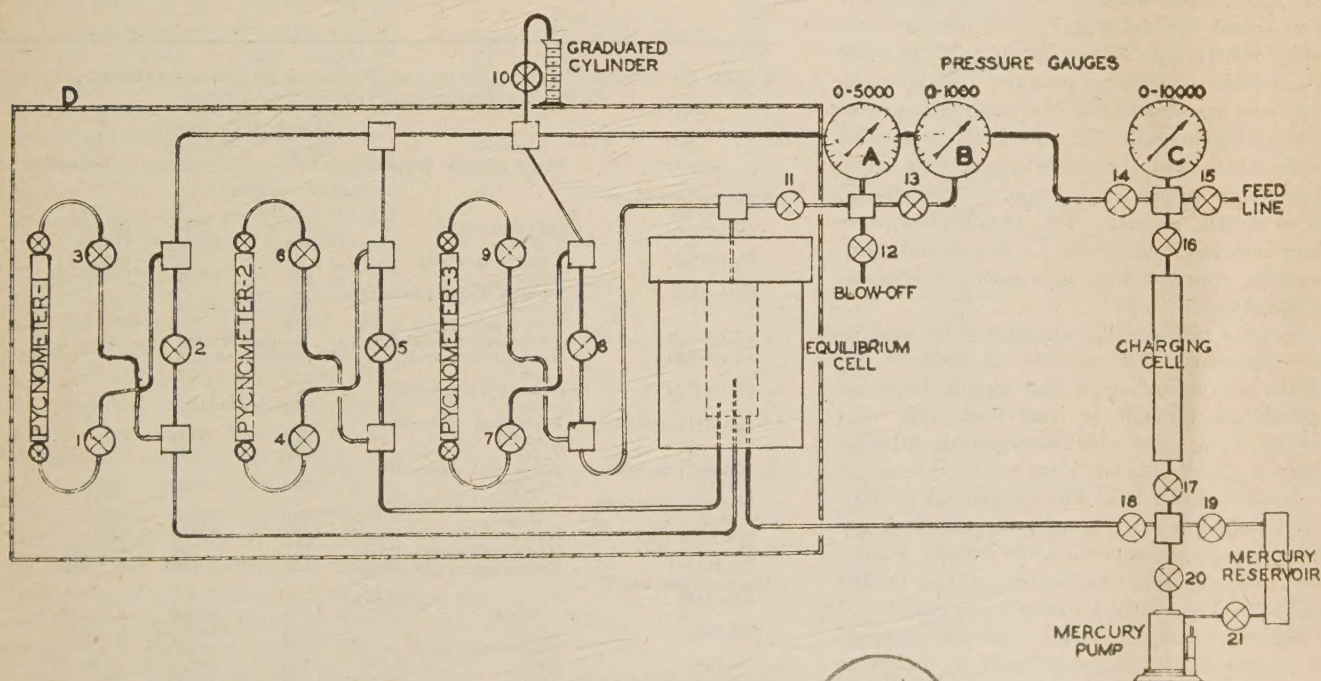


Figure 1. Apparatus



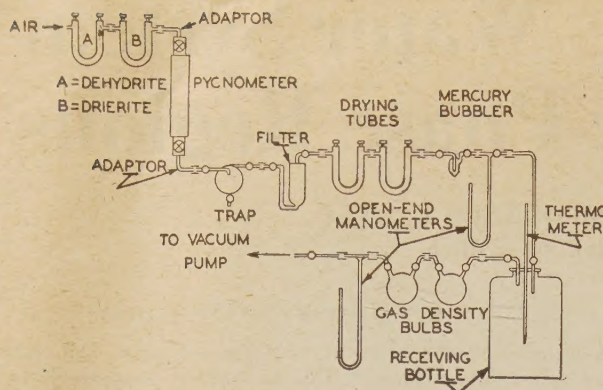


Figure 2. Analytical Train

square inch the pressure observations are believed to be within ± 2 pounds per square inch. Above this pressure the accuracy is believed to be within ± 5 pounds per square inch.

The following procedure was used to charge the equilibrium cell: The pycnometers and sampling lines were filled with mercury and their respective valves closed. The cell was first evacuated and flushed with methane two times, then filled with a predetermined amount of methane. The methane was added either directly from the cylinder or via the charging cell, depending upon the final pressure desired. The *n*-butane was added in a liquid form from a calibrated charging cell using mercury as a confining fluid. The water was measured into and added via the charging cell.

After the desired temperature was reached and the desired phases were observed to be present by means of the window, the temperature and pressure were held constant for a minimum of 3 hours, during which time the cell stirrer was operating intermittently. Approximately 15 minutes before sampling, the stirring within the cell was discontinued. In the three-phase investigation the hydrocarbon-rich liquid phase was sampled first into calibrated pycnometer 1. Valves 2 and 10 were opened slowly until all the mercury passed out into the graduated cylinder, then valve 2 was closed and valves 1 and 3 were opened as well as the needle valves on the pycnometer proper. Throughout the sampling period mercury was added slowly into the equilibrium cell in order to maintain the constant pressure. The pycnometer was maintained at the same pressure as the equilibrium cell. Samples of the water-rich liquid phase and the vapor phase were withdrawn into pycnometers 2 and 3, respectively, in a similar manner. The pycnometers were then removed and taken to a constant temperature, constant humidity room for analyses of the phases.

Figure 2 is a schematic diagram of the analytical apparatus. The method of analysis included the expanding of the sample from the pycnometer through an analytical train containing (a) a water and mercury trap, (b) filter made of glass beads and glass wool, (c) a pair of U-tubes filled with anhydrous magnesium perchlorate (Dehydrite), (d) a pair of calibrated gas density bulbs of approximately 200-cc. volume each, and (e) receiving bottles of the desired capacity. Essentially, the sample was dehydrated completely, and the dried gas was weighed in the gas density bulbs in order to determine the composition of the dried gas. The contents of the pycnometer were completely ex-

panded into a receiving bottle after passing through the analytical train, and then the gas was sampled from the receiving bottle where a single homogeneous phase was ensured. Pressures were read by means of an open-end monometer, and temperatures were read from mercury-in-glass thermometers. It is believed that the absolute pressures were read within ± 0.1 mm. of mercury of the true value. The analytical train and each of the receiving bottles, which ranged in volume from 1022 to 11,694 cc., were carefully calibrated. During the analysis of the vapor and hydrocarbon-rich liquid phases, the receiving volume was chosen so that the final pressure on the analytical apparatus would be as near 760 mm. as possible. For the water-rich phases no receiving bottles were used.

The pycnometers were weighed immediately after being removed from the equilibrium apparatus and were reweighed before an analysis was started; at no time did the second weighing show any loss of sample. Before the analysis the trap, adaptor, filter, and U-tubes were weighed after the stopcocks had been opened to the atmosphere. The gas density bulbs were weighed

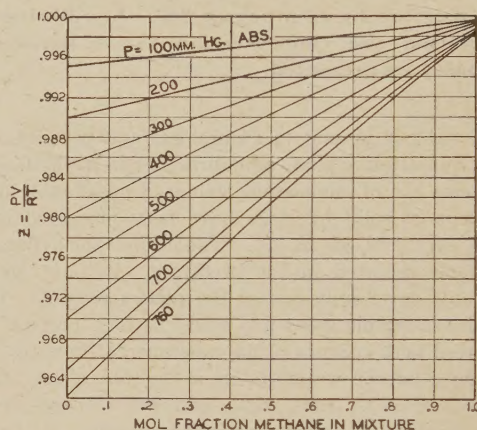
Figure 3. Compressibility Factors for Gaseous Mixtures of Methane and *n*-Butane at 70° F.

TABLE I. WATER-HYDROCARBON AND RELATED SYSTEMS INVESTIGATED AT ELEVATED PRESSURES AND TEMPERATURES

System	Phase Compn. Reported	Maximum Conditions		References
		Temp., ° F.	Pressure, lb./sq. in.	
Hydrocarbon-water systems				
CH ₄ -H ₂ O	H ₂ O-rich liquid	77	2350	(9, 50)
	Vapor	460	10000	(26)
C ₂ H ₆ -H ₂ O	P and T data only	89	710	(22)
	Vapor	460	10000	(30)
C ₃ H ₈ -H ₂ O	3-phase and 2-phase regions	300	3000	(5)
	Hydrocarbon-rich liquid	100	192	(14, 28)
C ₄ H ₁₀ -H ₂ O	Hydrocarbon-rich phases			
C ₅ H ₁₂ -H ₂ O	Over-all compositions only			
	3-phase critical			(31)
C ₆ H ₁₄ -H ₂ O	Over-all compositions only			
	3-phase critical			(40)
Natural gas-H ₂ O	Vapor and water-rich liquid			
		250	5000	(8)
Natural gas-NaCl-H ₂ O	Vapor and water-rich liquid	100	2000	(2, 7, 15, 23, 34)
Natural gas-glycol-H ₂ O	Vapor and glycol-rich liquid	250	5000	(8)
Naphtha-H ₂ O	Hydrocarbon-rich liquid	100	2000	(33)
Kerosene-H ₂ O	Hydrocarbon-rich liquid	431	370	(12)
Oil-H ₂ O	Hydrocarbon-rich liquid	507	750	(12, 13)
	Hydrocarbon-rich liquid	538	940	(12, 13)
Inorganic gas-water				
CO ₂ -H ₂ O	Vapor and water-rich liquid			
		212	10000	(45, 46, 47)
N ₂ -H ₂ O	Vapor	464	14700	(1, 36)
	Water-rich liquid	464	4500	(11, 35, 44, 48)
H ₂ -H ₂ O	Vapor	122	14700	(1, 29, 45)
H ₂ -N ₂ -H ₂ O	Vapor	122	14700	(1)
Air-H ₂ O	Vapor	100	1500	(25)

TABLE II. EXPERIMENTAL DATA IN THREE-PHASE REGION AT 100° F.

Run No.	Pressure, Lb./Sq. In. Abs.	Phase	Mol. Wt. Dry Gas	Mole Fraction ^a				Specific Vol., Cu.Ft./Lb.
				C ₁	C ₄	C ₁ + C ₄ in L _w	H ₂ O	
3B	631	V	21.40	0.8710	0.1290		0.00184	0.3935
		L _h	49.38	0.2076	0.7924		0.000338	0.03182
		L _w	19.51	0.000649	0.0000594	0.0007084	0.99929	0.01606
3C	202	V	25.04	0.7850	0.2150		0.00508	1.192
		L _h	55.20	0.0694	0.9306		0.000654	0.02895
		L _w	26.47	0.0002635	0.000087	0.0003505	0.9996495	0.01620
3D	1406	V	22.00	0.8580	0.1420		0.001028	0.1460
		L _h	39.15	0.4505	0.5495		0.000864	0.0383
		L _w	17.22	0.001505	0.000045	0.00155	0.99845	0.016095
3E	979	V	21.65	0.8650	0.1350		0.001315	0.2350
		L _h	45.20	0.3070	0.6930		0.000871	0.0332
		L _w	18.52	0.001051	0.000065	0.00116	0.998884	0.01621
3F	474	V	22.45	0.8470	0.1530		0.002315	0.5410
		L _h	51.90	0.1479	0.8521		0.000809	0.0320
		L _w	20.15	0.00072	0.000080	0.00080	0.9992	0.01648
3G	212	V	28.15	0.7125	0.2875		0.00485	1.060
		L _h	56.10	0.0480	0.9520		0.000692	0.02899
		L _w	22.10	0.000299	0.0000507	0.000349	0.99965	0.01625
3H	1838	V	23.80	0.8140	0.1860		0.000858	0.0870
		L _h	31.80	0.6240	0.3760		0.000824	0.0469
		L _w	16.77	0.001805	0.000033	0.001838	0.998162	0.1608
3I	1900	V	25.42	0.7770	0.2230		0.0008405	0.0715
		L _h	30.00	0.6690	0.3310		0.000831	0.0505
		L _w	16.72	0.001818	0.0000295	0.001848	0.99815	0.01610
3J	1910	V	26.65	0.7490	0.2510		0.000831	0.0665
		L _h	28.77	0.6975	0.3025		0.000832	0.0535
		L _w	16.62	0.01852	0.000028	0.00188	0.99812	0.0161
3K	1912	V	27.00	0.7390	0.2610		0.000835	0.06395
		L _h	28.12	0.7130	0.2870		0.000835	0.0550
		L _w	16.62	0.001852	0.000028	0.00188	0.99812	0.0161
3L	1880	V	24.25	0.8040	0.1960		0.000841	0.7785
		L _h	31.08	0.6420	0.3580		0.000828	0.0476
		L _w	16.72	0.001822	0.0000314	0.001853	0.99815	0.0161
3M	1220	V	21.18	0.8790	0.1210		0.00106	0.1802
		L _h	41.85	0.3860	0.6140		0.00082	0.0350
		L _w	17.82	0.00129	0.00006	0.00135	0.99865	0.01613

^a In V and L_h phases the mole fraction of C₁ and C₄ are given on the dry basis.

after evacuation to less than 0.1 mm. mercury absolute pressure. These were then placed on the analytical train with the desired receiving-bottle capacity and with the preweighed pycnometer containing the sample. The whole train, up to the pycnometer valve, was evacuated to approximately 0.1 mm. mercury absolute pressure. Temperatures and pressures were noted, the stopcock leading to the vacuum pump was closed, and the pycnometer valve was opened slowly. Approximately one half hour was allowed for the sample to be expanded. In the case of the hydrocarbon-rich liquid sample it was necessary to keep the pycnometer covered with a heating pad in order for the sample to emerge as a vapor. The expanded gas was allowed to remain in the train and receiving bottles until the temperature reached the constant room temperature of 70° F. The pressure and temperature were again noted and the gas density bulbs weighed. The difference in weight was assumed to be the weight of the dry gaseous mixture at the noted pressure and 70° F. Predried air was then passed through the pycnometer, adaptor, trap, filter, and U-tubes to remove any sample which may have remained in the pycnometer and also to displace the hydrocarbon gases from the train. The U-tubes were then reweighed with stopcocks bled to atmospheric pressure, and the increase in weight was assumed to be water. At no time was the increase in weight of the second U-tube in series greater than 1.0% of the increase of the weight of the first tube. The adaptor and trap were

next weighed, and the increase in weight was assumed to be mercury. Since, during the first fifty-four analyses, the filter neither gained nor lost weight, it was removed from the train in subsequent analyses. The pycnometer was weighed, and the loss in weight was assumed to be mercury plus wet sample.

Each of the weighings was done with a nearly identical tare, and the gain or loss in weight was determined by the substitution method. No correction was made for air buoyancy. It is believed that the weighings of the analytical apparatus were within ± 0.1 mg. and the weighing of the pycnometer within ± 5.0 mg.

Since actual gases do not follow the law of ideal gases even at atmospheric conditions, it was necessary to determine the volumetric behavior of gaseous mixtures of methane and *n*-butane. Figure 3 shows the smoothed compressibility factors at 70° F., based on fifty-six determinations at pressures from 100 to 760 mm. on three mixtures and the pure components. The data for the pure hydrocarbons agree fairly well with those in literature (18, 24, 27, 39), and the data for the gaseous mixtures

at 760 mm. agree fairly well with those of Sage, Hicks, and Lacey (38).

Before any runs were made on the methane-*n*-butane-water system, data were obtained on the binary mixtures methane-water and methane-*n*-butane at several temperatures and pressures. The compositions found checked those of the literature (26, 38) within $\pm 1.0\%$. A check on the analytical results was

TABLE III. EXPERIMENTAL DATA IN THREE-PHASE REGION AT 160° F.

Run No.	Pressure, Lb./Sq. In. Abs.	Phase	Mol. Wt. Dry Gas	Mole Fraction ^a				Vol., Cu.Ft./Lb.
				C ₁	C ₄	C ₁ + C ₄ in L _w	H ₂ O	
4A	1683	V	26.89	0.7425	0.2575		0.0038	0.0912
		L _h	36.63	0.5105	0.4895		0.0035	0.0455
		L _w	17.98	0.00149	0.00072	0.001562	0.99844	0.1631
4B	1479	V	25.28	0.7810	0.2190		0.004295	0.1190
		L _h	39.70	0.4380	0.5620		0.0035	0.0420
		L _w	18.10	0.00135	0.00001	0.00142	0.99858	0.01640
4C	1022	V	24.64	0.7960	0.2040		0.00539	0.2000
		L _h	45.75	0.2938	0.7062		0.00309	0.0369
		L _w	19.60	0.00099	0.000091	0.00108	0.99892	0.01648
Lost Sample								
4D	535	V						
		L _h	52.45	0.1348	0.8652		0.0030	0.0330
		L _w	22.75	0.00052	0.000098	0.000618	0.99938	0.01665
4E	192	V	44.00	0.3360	0.6640		0.02210	0.8135
		L _h	57.00	0.0266	0.9734		0.00242	0.0317
		L _w	55.32	0.000015	0.00021	0.000225	0.99977	0.01650
4F	1635	V	25.72	0.7695	0.2305		0.00398	0.09925
		L _h	37.20	0.4965	0.5035		0.00352	0.0455
		L _w	17.82	0.001462	0.000064	0.001526	0.99847	0.01636
4G	1729	V	27.98	0.7155	0.2845		0.00366	0.0830
		L _h	35.70	0.5330	0.4670		0.00355	0.0480
		L _w	17.73	0.001535	0.000064	0.001599	0.9984	0.01636
4H	1051	V	24.48	0.7990	0.2010		0.00538	0.1995
		L _h	45.60	0.2975	0.7025		0.00327	0.0380
		L _w	21.12	0.000975	0.000133	0.001108	0.99889	0.01638
4I	1796	V	30.15	0.6645	0.3355		0.00354	0.0725
		L _h	33.76	0.5895	0.4205		0.00370	0.0530
		L _w	17.30	0.001585	0.000048	0.001633	0.99863	0.01637
4J	604	V	26.78	0.7445	0.2554		0.00782	0.3400
		L _h	51.53	0.1568	0.8432		0.00280	0.0340
		L _w	25.68	0.000555	0.000165	0.000720	0.99928	0.01642
4K	1810	V	30.80	0.6475	0.3525		0.00359	0.0700
		L _h	32.88	0.60000	0.40000		0.00360	0.0550
		L _w	17.22	0.001602	0.000046	0.001648	0.99835	0.01633

^a In V and L_h phases the mole fraction of C₁ and C₄ are given on the dry basis.

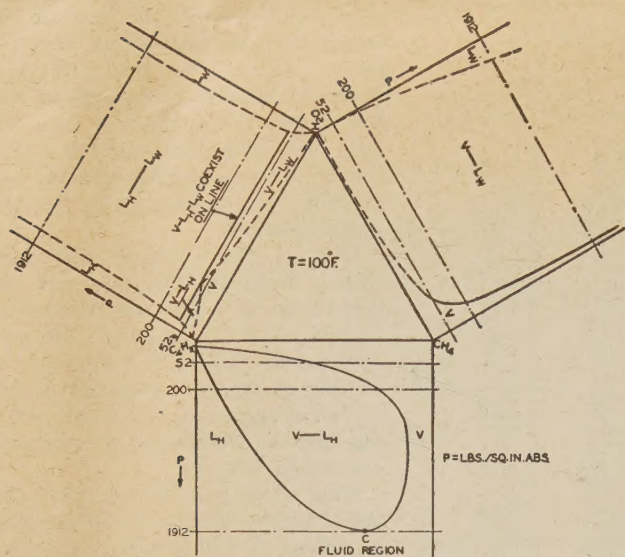


Figure 4. Pressure-Composition Diagrams of Binary Mixtures at 100° F.

agreement between the calculated content of the pycnometer and the weighed content within 0.1% or better, in 95% of the cases.

MATERIALS USED. The hydrocarbons employed in this investigation were furnished through the courtesy of the Phillips Petroleum Company. The methane was stated to have a purity of 99.9 mole %, and the *n*-butane 99.9 mole % or better. Each gas was passed through a train containing granular calcium chloride, sodium hydroxide activated charcoal, Ascarite, and magnesium perchlorate, at cylinder pressure, in order to remove minute impurities present which would adsorb on the Dehydrite. The water was redistilled in an atmosphere of methane, stored in a container under methane pressure, and transferred to the equilibrium cell without contact with air.

EXPERIMENTAL RESULTS

The experimental data obtained in this investigation are presented in Tables II to VI. The molecular weight of dry gas represents the hydrocarbon composition on a water free basis.

Figure 4 shows the pressure-composition diagrams at 100° F. of the three binary systems previously investigated: methane-water (26), *n*-butane-water (31), and methane-*n*-butane (38).

Complete data on the first two binary systems mentioned have not been presented, and the missing data are shown by broken lines. By following the lines of constant pressure on the three binary systems the terminal data of the ternary system may be determined.

Figure 5 shows schematic ternary diagrams at 100° F. at the various pressures. The phase boundary lines are greatly exaggerated in order that they do not coincide with the sides of the triangular diagram. The compositions within the triangular diagrams of Figure 5 cannot be predicted from the binary diagrams of Figure 4. One rule, however, can be followed; all of the phase equilibria that appear in the binary systems at a given temperature and pressure must

exist in the ternary system at the same temperature and pressure (4). With this rule as a guide a general qualitative view of the ternary diagram may be obtained at a given pressure and temperature from the three binary systems.

Figure 5A, at 52 pounds per square inch absolute, shows the existence of two two-phase regions, one a vapor phase in equilibrium with a water-rich liquid phase, and the second, a vapor phase (the same vapor) in equilibrium with a hydrocarbon-rich liquid phase. No data were obtained in this region during this investigation. However, Figure 4 shows the pressure of 52 pounds per square inch absolute is higher than the vapor pressure of pure *n*-butane but lower than the pressure of the three coexisting phases of the *n*-butane-water system at 100° F. At this pressure in the *n*-butane-water system, two two-phase regions appear, a vapor phase in equilibrium with a water-rich liquid phase, and a vapor (the same vapor) in equilibrium with a butane-rich liquid phase. In the methane-water system at this pressure only one two-phase region appears, a vapor phase in equilibrium with a water-rich liquid phase. In the methane-*n*-butane system at this pressure only one two-phase region appears, a vapor phase in equilibrium with a butane-rich liquid phase. Therefore, by use of the rule mentioned, in the triangular diagram at 100° F. and 52 pounds per square inch absolute two two-phase regions must appear, one which represents equilibrium between vapor and water-rich liquid, and the second, between vapor and butane-rich liquid.

Triangular diagram B of Figure 5 is at a pressure corresponding to three types of two-phase equilibria: hydrocarbon-rich liquid (L_H)-water-rich liquid (L_W), vapor- L_H , and $V-L_W$, and one three-phase equilibrium, L_H-L_W-V . At a corresponding pressure

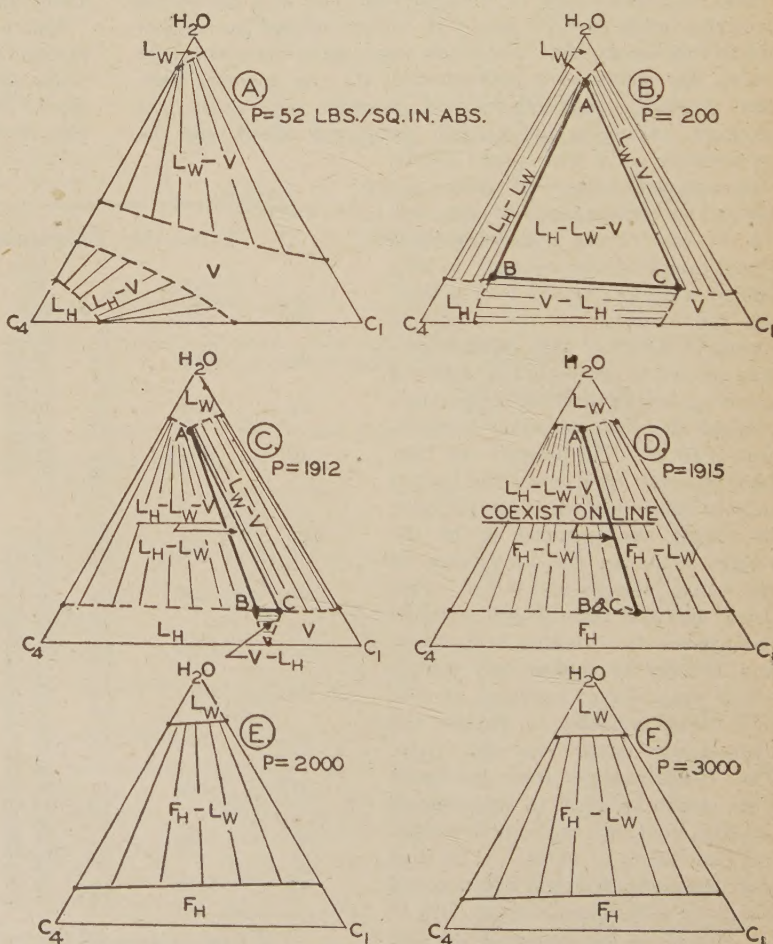


Figure 5. Ternary Isobars at 100° F.

in Figure 4 all of these two-phase equilibria are present. Points *A*, *B*, and *C* in Figure 5*B* represent the coexisting L_w , L_h , and vapor phases, respectively. The triangular area bounded by

ABC is called the three-phase region. The composition of the coexisting L_w , L_h , and V phases are represented by the points *A*, *B*, and *C*, respectively, for any over-all composition within the three-phase region.

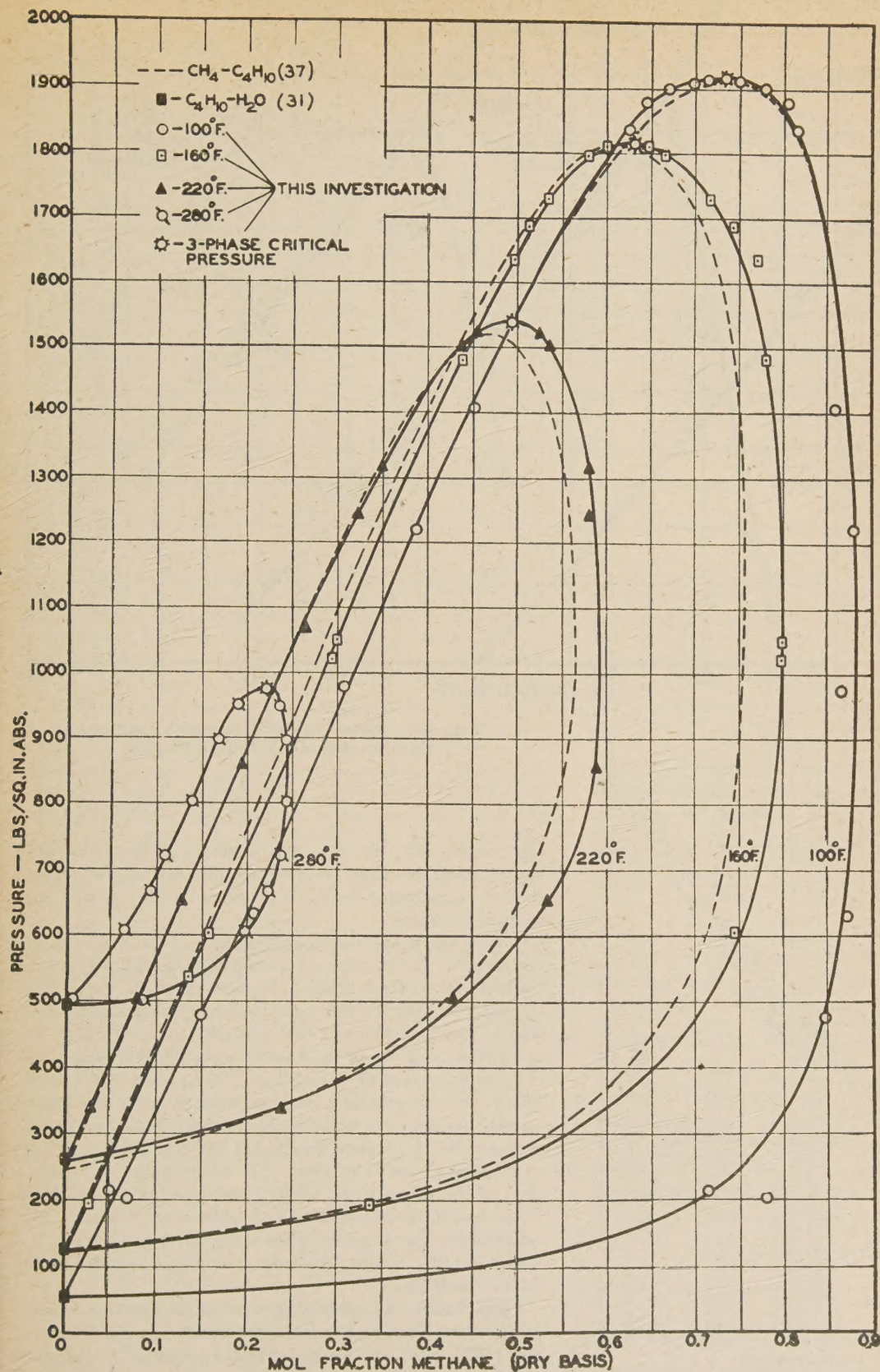


Figure 6. Effect of Water on Vapor-Liquid Equilibrium of Methane-*n*-Butane System

Figure 5*C*, 1912 pounds per square inch absolute, corresponds to the critical pressure of the methane-*n*-butane system. Within the triangular diagram a three-phase region is still present. With a slight increase in pressure, say to 1913 pounds per square inch absolute, the methane-*n*-butane system exists only in a single fluid phase (at 100° F.).

The three-phase region persists up to 1915 pounds per square inch absolute, at which pressure (100° F.) the phases L_h and V become identical. This pressure is called here the three-phase critical pressure. Above this pressure only one two-phase region appears. The critical pressure of this single two-phase region is beyond the scope of this investigation and is well above 3000 pounds per square inch, the maximum experimental pressure. Figures 5*E* and 5*F* show the two-phase region at 2000 and 3000 pounds per square inch absolute, respectively. The compositions and specific volumes of the phases in equilibrium in this region appear in Table VI. The various isobars of Figure 5 may be placed directly above one another at the proper pressure spacing to give the familiar ternary pressure-composi-

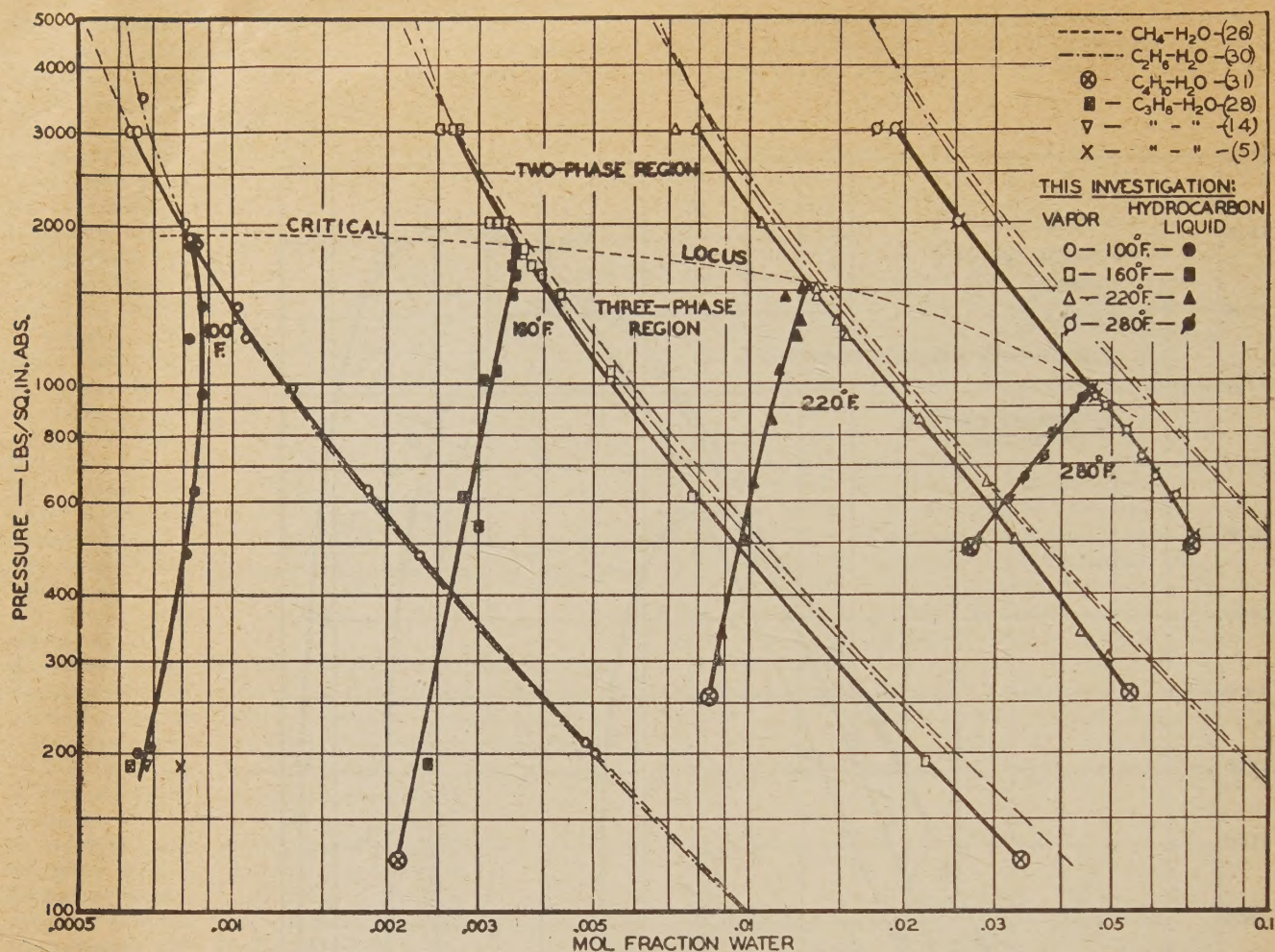


Figure 7. Solubility of Water in Vapor and Hydrocarbon-Rich Liquid Phases

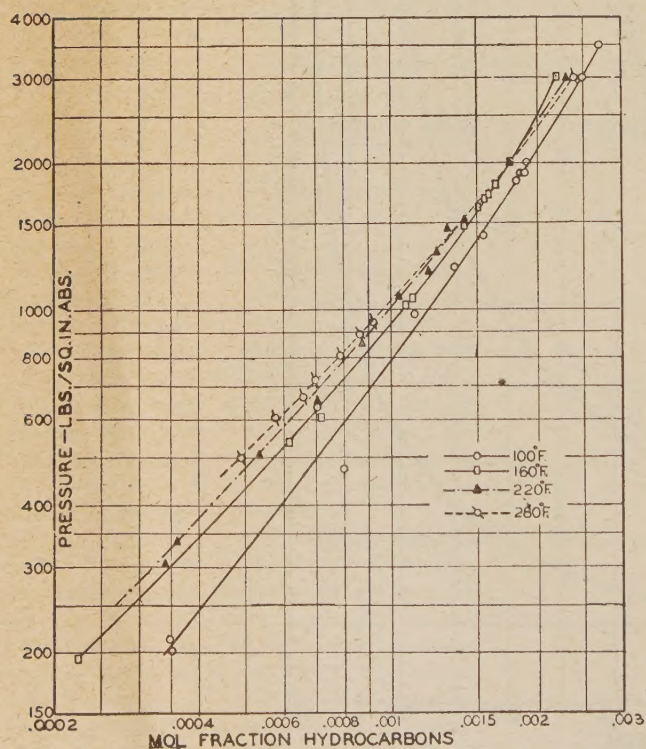


Figure 8. Solubility of Total Hydrocarbons in Water-Rich Liquid Phase

tion diagram at 100° F. The existence of the three-phase region, three two-phase regions, and three single-phase regions, however, complicates the figure to such an extent that its presentation is omitted.

A more useful and clearer presentation of the results of this investigation may be made by the use of isothermal and isobaric sections of the various phases. Figure 6 shows the vapor-liquid equilibria between the vapor and hydrocarbon-rich liquid phases as a function of pressure (at 100°, 160°, 220°, and 280° F.). The composition is given on the water-free basis. The broken lines of Figure 6 represent the data of Sage, Hicks, and Lacey (38) on the system methane-*n*-butane. The presence of water has little or no effect on the vapor-liquid equilibria of the methane-*n*-butane system at 100° F., whereas the effect at 160° and 220° F. is as high as 8% on the basis of methane. The results indicate the magnitude of the errors which would occur in hydrocarbon vapor-liquid equilibria determinations if water were present. It is believed that the accuracy of the smoothed data of Figure 6 is within $\pm 1.0\%$. Table VII shows the effects of water on the critical conditions.

Figure 7 shows the effect of pressure on the solubility of water in the vapor phase and in the hydrocarbon-rich liquid phase at 100°, 160°, 220°, and 280° F. The data of other investigations are also shown. The water content of the vapor is always higher than the water content of the equilibrium hydrocarbon-rich

TABLE IV. EXPERIMENTAL DATA IN THREE-PHASE REGION AT 220° F.

Run No.	Pressure, Lb./Sq. In. Abs.	Phase	Mol. Wt. Dry Gas	Mole Fraction ^a				Vol., Cu. Ft./Lb.
				C ₁	C ₄	C ₁ + C ₄ in L _w	H ₂ O	
5A	1241	V	33.75	0.5790	0.4210		0.01535	0.1103
		L _h	44.64	0.3202	0.6898		0.01238	0.04805
		L _w	23.22	0.000998	0.000205	0.001203	0.9988	0.01675
		V	33.85	0.5770	0.4230		0.01485	0.1002
5D	1316	L _h	43.50	0.3476	0.6524		0.01255	0.0481
		L _w	21.42	0.001091	0.000156	0.001247	0.99875	0.01679
		Lost Sample						
5E	1066	L _h	47.10	0.2620	0.7380		0.01148	0.0431
		L _w	20.87	0.000929	0.000119	0.001048	0.99895	0.01673
5F	855	V	33.42	0.5875	0.4125		0.02145	0.1722
		L _h	50.05	0.1918	0.8082		0.01108	0.04065
		L _w	28.20	0.000626	0.000256	0.000882	0.99912	0.01688
5G	500	V	40.15	0.4268	0.5732		0.0324	0.2854
		L _h	54.86	0.0775	0.9225		0.0098	0.03705
		L _w	36.88	0.00027	0.000266	0.000536	0.99946	0.01685
5H	338	V	48.10	0.2380	0.7620		0.04365	0.3510
		L _h	57.00	0.0267	0.9733		0.00882	0.0370
		L _w	36.50	0.000185	0.000175	0.00036	0.99964	0.01677
5I	1520	V	36.04	0.5245	0.4755		0.01298	0.0722
		L _h	39.00	0.4545	0.5455		0.01288	0.541
		L _w	19.00	0.001304	0.000098	0.001402	0.9986	0.01678
5J	1460	V	34.76	0.5550	0.4450		0.0136	0.0811
		L _h	40.80	0.4105	0.5895		0.01172	0.05215
		L _w	20.50	0.00117	0.000137	0.001307	0.9987	0.01672
5K	651	V	35.65	0.5335	0.4665		0.0287	0.2305
		L _h	52.80	0.1264	0.8736		0.102	0.03908
		L _w	27.30	0.00052	0.00019	0.00071	0.99929	0.01677
5L	301	V	51.32	0.1618	0.8382		0.0494	0.3520
		L _h	57.47	0.01555	0.9845		0.0088	0.03605
		L _w	51.32	0.00005	0.000286	0.000341	0.99966	0.01683
5M	1499	V	35.60	0.5350	0.4650		0.01348	0.0781
		L _h	39.77	0.4360	0.5640		0.01276	0.05402
		L _w	20.03	0.001258	0.0001305	0.00139	0.99861	0.01675

^a In V and L_h phases the mole fraction of C₁ and C₄ are given on the dry basis.

liquid. This has also been shown by Griswold and Kasch (12). The water content of the vapor phase and the hydrocarbon-rich liquid phase is shown to be identical at the three-phase critical pressure; this is to be expected, since at this critical pressure the vapor phase and hydrocarbon-rich liquid phase are identical phases. The solubility of water in the vapor phase was found to be dependent upon the molecular weight of the vapor, ranging from methane to butane. The water concentration of the hydrocarbon-rich liquid for the propane-water system (5, 14, 28) at 100° F. is in agreement with the methane-*n*-butane-water system.

Figure 8 shows the effect of pressure on the solubility of the total hydrocarbons (methane plus *n*-butane) in the water-rich liquid phase at 100°, 160°, 220°, and 280° F. In Figure 9 these

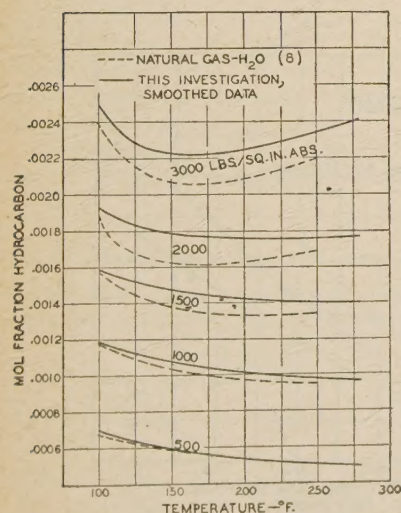


Figure 9. Solubility of Total Hydrocarbons in Water Exhibiting Minimum Solubility

data are cross-plotted to show better the minimum solubility at higher pressures. The broken lines of Figure 9 are Dodson and Standing's data on the solubility of natural gas in water (8). Minimum solubilities have been observed in various systems (8, 11, 19, 21, 35, 50). Winkler (50) and Kuenen (21) explained this phenomenon of minimum solubility as a neutralization effect of the opposing factors of viscosity and thermal expansion of the liquid.

Figure 10 shows the effect of pressure on the solubility of the individual hydrocarbons in the water-rich liquid phase. Because of the small amount of sample analyzed and the slight solubility of the hydrocarbons in the water-rich liquid phase, the composition of these gases was determined at pressures far below atmospheric pressure. Therefore the data of Figure 10 are not believed to be highly accurate. It is interesting, however, that water has a greater affinity for methane than for *n*-butane even when the phase in equilibrium with the water-rich liquid phase is considerably richer in *n*-butane.

The specific volumes of the vapor phase and the hydrocarbon-rich liquid phases in the three-phase region are shown in Figure 11 as a function of pressure at 100°, 160°, 220°, and 280° F. Included in Figure 11 are the specific volumes of the methane-*n*-butane vapor and liquid phases as reported by Sage, Hicks, and Lacey (38). In Figure 12 are plotted the specific volumes of the hydrocarbon-rich fluid phases in the two-phase region of the methane-*n*-butane-water system at 3000 pounds per square inch absolute as a function of the composition of the phase (water-free basis). The solid lines represent the results of Sage, Budenholzer, and Lacey (37) on the methane-*n*-butane system in the single-phase region, and the plotted points show the results of this investigation. The effect of water on the specific volume of the hydrocarbon-rich fluid phase is negligible in this region. Figure 13 shows the effect of pressure on the specific volume of the water-rich liquid in the two- and three-phase regions. The broken lines represent the specific volume of pure water (20), and

TABLE V. EXPERIMENTAL DATA IN THREE-PHASE REGION AT 280° F.

Run No.	Pressure, Lb./Sq. In. Abs.	Phase	Mol. Wt. Dry Gas	Mole Fraction ^a				Specific Vol., Cu. Ft./Lb.
				C ₁	C ₄	C ₁ + C ₄ in L _w	H ₂ O	
6A	665	V	48.78	0.2220	0.7780		0.0606	0.1291
		L _h	54.31	0.0906	0.9094		0.0341	0.0475
		L _w	39.78	0.000286	0.00037	0.000656	0.999344	0.01730
6B	895	V	48.00	0.2406	0.7594		0.0485	0.0930
		L _h	51.05	0.1680	0.8320		0.04285	0.0550
		L _w	35.82	0.000455	0.000405	0.00086	0.99914	0.01734
6C	720	V	48.20	0.2358	0.7642		0.05725	0.1182
		L _h	53.64	0.1067	0.8933		0.03705	0.0510
		L _w	35.58	0.000375	0.000325	0.00070	0.99930	0.01722
6D	500	V	54.60	0.0836	0.9164		0.0718	0.1600
		L _h	57.90	0.0053	0.9947		0.0274	0.04605
		L _w	52.98	0.00006	0.00043	0.0049	0.99951	0.09735
6E	948	V	48.24	0.2348	0.7652		0.0439	0.0848
		L _h	50.21	0.1880	0.8120		0.0456	0.05904
		L _w	33.00	0.00055	0.00037	0.00092	0.99908	0.01729
6F	805	V	47.92	0.2428	0.7572		0.0536	0.1010
		L _h	52.32	0.1378	0.8622		0.03815	0.05102
		L _w	33.62	0.00046	0.00033	0.00079	0.99921	0.01727
6G	608	V	49.80	0.1977	0.8023		0.066	0.1381
		L _h	55.50	0.0624	0.9376		0.0318	0.04795
		L _w	53.78	0.00006	0.00052	0.00058	0.99942	0.01733

^a In V and L_h phases the mole fraction of C₁ and C₄ are given on the dry basis.

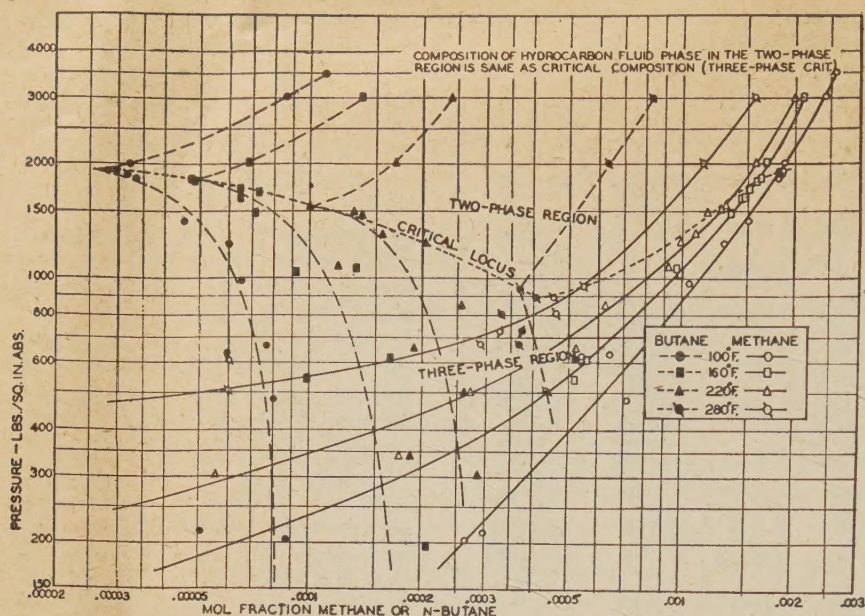


Figure 10. Solubility of Individual Hydrocarbons in Water-Rich Liquid Phase

the dissolved hydrocarbons appear to increase the specific volume of the water-rich liquid less than 0.5%.

EQUILIBRIUM CONSTANTS

In a ternary system in the two-phase region there are three sets of equilibrium constants. For component *a* this familiar relation is Equation 1.

$$K_a = \frac{x_{aV}}{x_{aL}} \quad (1)$$

In a ternary system in the three-phase region, however, there are three sets of equilibrium constants or composition ratios for each component. For component *a* these relations are:

$$K'_a = \frac{x_{aV}}{x_{aL_h}} \quad (2)$$

$$K''_a = \frac{x_{aV}}{x_{aL_w}} \quad (3)$$

$$K'''_a = \frac{x_{aL_h}}{x_{aL_w}} \quad (4)$$

Equations 3, 4, and 5 are not independent, however, since $K'_a = K'_a K'''_a$.

Figure 14 shows the experimental values for the equilibrium constants of methane and *n*-butane between the hydrocarbon fluid and water-rich liquid in the two-phase region as a function of concentration of the hydrocarbon-rich liquid phase at 2000 and 3000 pounds per square inch absolute. The equilibrium constants for both methane and *n*-butane may be assumed to be essentially independent of temperature but vary with pressure and composition of the hydrocarbon-rich phase.

Figures 15 and 16 show the equilibrium constants of methane, *n*-butane, and water between the vapor and hydrocarbon-rich liquid as a function of pressure at temperatures of 100°, 160°, 220°, and 280° F. in the three-phase region. The data of the methane-*n*-butane system (38) and the *n*-butane-water system (31) are plotted. Although *n*-butane has a higher vapor pressure than water at a given temperature, water is the more volatile of the two components in this system.

Figure 17 shows the equilibrium constants of methane, *n*-butane, and water at 160° F. as a function of pressure in the three-phase and two-phase regions. This figure was prepared from the smoothed data of Figures 6, 7, 10, and 14.

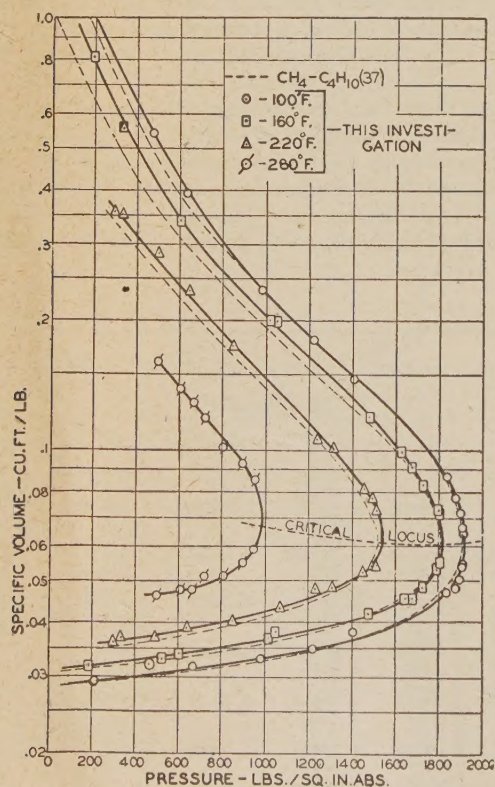


Figure 11. Specific Volume of Vapor and Hydrocarbon-Rich Liquid in Three-Phase Region

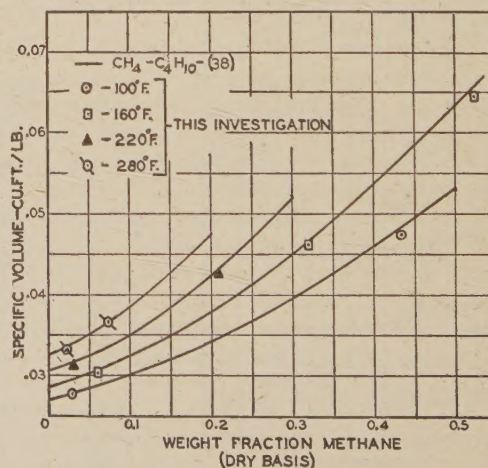


Figure 12. Specific Volume of Hydrocarbon-Rich Phase at 3000 Pounds per Square Inch Absolute in Two-Phase Regions

TABLE VI. EXPERIMENTAL DATA IN TWO-PHASE REGION

Run No.	Temp., ° F.	Pressure, Lb./Sq. In. Abs.	Phase	Mol. Wt. Dry	Mole Fraction ^a			H ₂ O	Specific Cu. Ft./Lb.
					C ₁	C ₄	C ₁ + C ₄ in L _w		
3A	100	3520	F _h	27.15	0.7360	0.2640		0.000656	0.0438
			L _w	17.70	0.00259	0.00011	0.0027	0.9973	0.01596
10A	100	2996	F _h	27.3	0.7325	0.2675		0.00065	0.0474
			L _w	17.50	0.002414	0.000086	0.0025	0.9975	0.01604
10B	100	1998	F _h	27.40	0.7310	0.2690		0.000804	0.06025
			L _w	16.87	0.01868	0.000032	0.0019	0.9981	0.01606
10C	100	2996	F _h	54.35	0.0896	0.9104		0.000639	0.02755
			L _w	44.50	0.00081	0.00169	0.0025	0.9975	0.01600
7A	160	3018	F _h	31.60	0.6300	0.3700		0.00274	0.04600
			L _w	31.55	0.6302	0.3698		0.00328	0.05795
7B	160	2048	F _h	17.72	0.001682	0.000068	0.00175	0.99825	0.01635
			L _w	24.50	0.795	0.2005		0.00270	0.06440
7C	160	2948	F _h	17.22	0.002158	0.000062	0.00222	0.99778	0.01626
			L _w	24.48	0.7996	0.2004		0.00339	0.08725
7D	160	1988	F _h	16.72	0.001724	0.000026	0.00175	0.99825	0.01635
			L _w	50.10	0.1905	0.8095		0.00254	0.0302
7E	160	2998	F _h	33.10	0.00132	0.0009	0.00222	0.99778	0.01627
			L _w	50.25	0.1874	0.8126		0.00316	0.03214
7F	160	1990	F _h	32.4	0.00107	0.00068	0.00175	0.99825	0.01629
			L _w	37.44	0.4915	0.5085		0.00795	0.0425
8A	220	2998	F _h	20.42	0.00208	0.00024	0.00232	0.99768	0.01664
			L _w	37.28	0.4945	0.5055		0.01056	0.05245
8B	220	1999	F _h	20.22	0.00158	0.00158	0.00175	0.99825	0.01670
			L _w	54.30	0.0908	0.9092		0.00718	0.0312
8C	220	2996	F _h	45.62	0.00073	0.00173	0.00246	0.99754	0.01665
			L _w	48.9	0.2190	0.7810		0.0193	0.0365
9A	280	2998	F _h	30.6	0.00157	0.00083	0.00240	0.9976	0.01710
			L _w	48.9	0.2190	0.7810		0.0253	0.0399
9B	280	1999	F _h	31.0	0.00113	0.00063	0.00176	0.99824	0.01722
			L _w	54.9	0.0765	0.9235		0.0177	0.03325
9C	280	2998	F _h	47.6	0.00061	0.00184	0.00245	0.99755	0.01715
			L _w						

^a In F_h phase the mole fraction of C₁ and C₄ are given on the dry basis.

The phase rule of Gibbs (10) shows that in a ternary system with three phases coexisting in equilibrium the degree of variance is 2. Therefore, if the temperature and pressure are fixed and the system is in the three-phase region, the compositions of the three phases are fixed; hence the equilibrium constants are fixed. This can be seen from Figure 17. At pressures below 1815 pounds per square inch absolute (the three-phase critical pressure at 160° F.), the equilibrium constants, between the vapor and hydrocarbon-rich liquid and between the hydrocarbon-rich liquid and water-rich liquid, are independent of the composition of the over-all system, as long as the three phases are present.

In a ternary system with two phases co-existing in equilibrium, however, the degree of variance is 3. Therefore, in addition to the temperature and pressure, a third variable must be specified in order to define the system completely. In Figure 17 the third specification imposed is the concentration of the hydrocarbon-fluid phase. In an ideal system in the two-phase region the equilibrium constant is independent of the composition, but in this investigation the components do not behave ideally. The equilibrium constants for butane in Figure 17 also are dependent on the composition but are not shown. These latter constants may be obtained from Figure 14.

An additional equilibrium constant is shown in Figure 17—that of the total hydrocarbons—which is equal to the mole

fraction of the total hydrocarbons in the vapor phase divided by the mole fraction of the total hydrocarbon dissolved in the water-rich liquid phase, all on a water-free basis. This last equilibrium constant is in good agreement with that of the natural gas-water system (8).

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NOMENCLATURE

a = one component in any phase
F_h = hydrocarbon-rich fluid phase
L_h = hydrocarbon-rich liquid phase

L_w = water-rich liquid phase
V = vapor phase
x_{aV} = mole fraction of component *a* in the vapor phase
x_{aL_h} = mole fraction of component *a* in hydrocarbon-rich liquid phase
x_{aL_w} = mole fraction of component *a* in water-rich liquid phase

TABLE VII. EFFECT OF WATER ON CRITICAL PRESSURE AND CRITICAL COMPOSITION OF METHANE-*n*-BUTANE SYSTEM

Temp., ° F.	Critical Pressure, Lb./Sq. In. Abs.		Critical Compn., Mole Fraction Methane	
	C ₁ - <i>n</i> -C ₄ , 2-phase, critical	C ₁ - <i>n</i> -C ₄ -H ₂ O, 3-phase, critical	C ₁ - <i>n</i> -C ₄ , 2-phase, critical	C ₁ - <i>n</i> -C ₄ -H ₂ O ^a , 3-phase, critical
100	1912	1915	0.7230	0.7320
160	1810	1815	0.6150	0.6300
220	1520	1540	0.4720	0.4925
280	910 ^b	970	0.2000 ^b	0.2190

^a Dry basis.

^b Extrapolated.

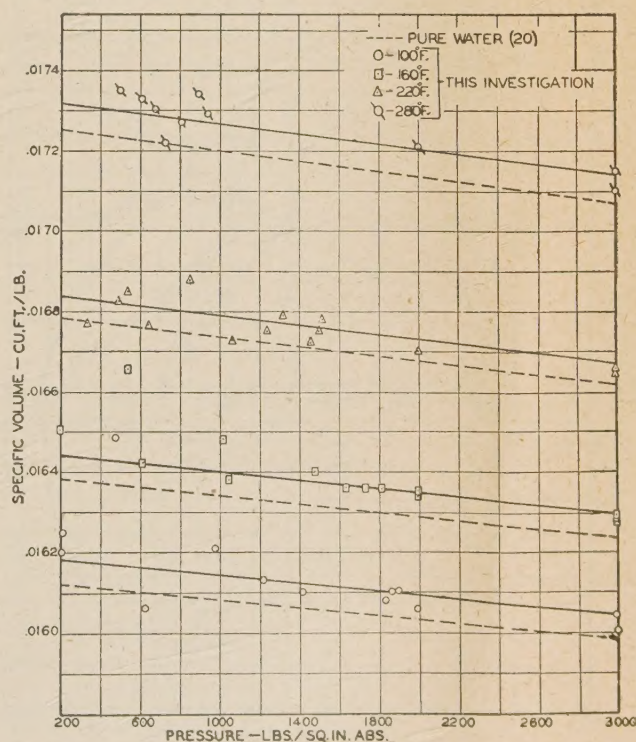


Figure 13. Specific Volume of Water-Rich Liquid Phase in Two- and Three-Phase Regions

